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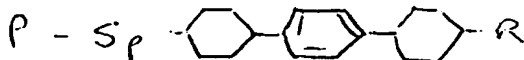
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(54) Abstract Title
1,4-di-(trans-cyclohexyl)benzenes

(57) The invention relates to a polymerisable liquid crystal material comprising at least one polymerisable surface-active compound, its use for the preparation of anisotropic polymer films, and the use of the liquid crystal material and the polymer films in optical and electrooptical devices, for decorative and security applications.

The compounds are of formula



P is a polymerisable group especially alkenyl

Sp is a spacer group especially (CH₂)_n-O

R is a substituent but especially P-O-(CH₂)_n and the benzene ring is optionally substituted especially by fluorine.

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Polymerisable Dicyclohexylbenzenes

Field of the Invention

5 The invention relates to polymerisable mesogenic or liquid crystalline 1,4-di-(trans-cyclohexyl)benzenes, to polymerisable mesogenic or liquid crystalline mixtures and anisotropic polymers prepared thereof, and to the use of the 1,4-di-(trans-cyclohexyl)benzenes and the mixtures and polymers prepared thereof in optical and electrooptical
10 devices, adhesives, synthetic resins with anisotropic mechanical properties, cosmetics, diagnostics, liquid crystal pigments, decorative and security applications, nonlinear optics, optical information storage, electronic devices like organic field effect transistors (FET or OFET), electroluminescent devices, or as chiral dopants.

15

Background and Prior Art

Polymerisable mesogenic or liquid crystalline compounds, which are also known as reactive mesogenic compounds, have been described
20 in prior art for various purposes. For example, they can be aligned in their liquid crystal phase and subsequently polymerized in situ to give linear or crosslinked liquid crystal polymer films with uniform orientation of high quality. These films can be used as optical elements like polarisers or compensators in flat panel displays, as
25 described for example in EP 0 397 263, EP 0 606 940 WO 97/35219, WO 98/00475, WO 98/04651 or WO 98/12584.

Polymerisable mesogenic compounds have also been suggested for use in polymerised cholesteric liquid crystal films or coatings that
30 show selective reflection of visible light and are suitable as optical films and for preparation of liquid crystal pigments, as described for example in WO 97/30136. Another important field of use are security markings as described for example in US 5,678,863, or hot stamping foils as described for example in GB 2,357,061.

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Further to the use as optical films in displays, polymerisable mesogenic compounds have been suggested for use in the active, switchable layer of a liquid crystal display.

- 5 For example, displays are known which are switched between transparent and scattering states and comprise a low molar mass liquid crystal (LC) medium and a phase-separated polymerised liquid crystal material, like for example PDLC (polymer dispersed liquid crystal) displays as described in WO 93/22397, or polymer gel or
10 polymer network displays of the scattering type, as described in US 5,538,768, US 5,543,075 or EP 0 451 905.

- Furthermore, displays are known wherein a low molar mass LC medium is switched between two non-scattering states, like
15 conventional displays of e.g. the TN or STN, ECB, VA or IPS mode, and which further comprise a polymerised liquid crystal material in order to create a multidomain structure to improve the contrast at wide viewing angles or to stabilise the different switching states in order to reduce the driving voltage and the switching times. Such
20 displays are described for example in US 5,189,540, US 6,177,972, EP 0 903 392, and Hasebe et al., Jpn.J.Appl.Phys.1994, 33, 6245.

- For the above applications, usually mixtures of two or more polymerisable mesogenic compounds are used, as they have lower
25 melting points and broader liquid crystal phases than single compounds. It is desired to have available polymerisable mixtures exhibiting a liquid crystal phase, preferably a nematic or chiral nematic phase, at room temperature, so that it is possible to carry out alignment and polymerisation at low temperatures. For this
30 purpose, it is advantageous if the single polymerisable compounds do already exhibit broad liquid crystalline phases.

- For use in the switchable layer of liquid crystal displays, where they are typically mixed with a low molar mass LC medium, it is often
35 required that the polymerisable mesogenic compounds have properties, like the liquid crystal phase range and birefringence, that

are similar to those of the LC medium. When used in switchable displays that are not of the scattering type, and where the polymerised material is not macroscopically phase separated from the low molar mass LC medium, the polymerisable compounds
5 should preferably show good miscibility with the LC medium.

The polymerisable mesogenic compounds described in prior art, however, do often exhibit liquid crystalline phases only in a small temperature range or do not show mesophase behaviour at all.
10 Furthermore, they often show poor solubility in low molar mass LC media and have unfavourable values of the birefringence that are e.g. too high or too low.

Thus, there is a demand for polymerisable mesogenic compounds with a broad liquid crystalline phase which can be used for the preparation of oriented liquid crystal polymer films. In particular there is a demand for polymerisable mesogenic compounds that are suitable for use in the active layer of switchable LC devices in admixture with low molar mass LC media, have broad liquid crystal
15 20 phases preferably at room temperature, have properties adapted to those of the LC media, and show good solubility on the LC media.

Furthermore, regarding the broad range of applications for polymerisable mesogenic compounds it is desirable for the expert to have available further compounds of this type which are easy to synthesize and fulfill the various requirements as described above.
25

It was an aim of the invention to provide polymerisable mesogenic compounds with the advantageous properties mentioned above, thus extending the pool of polymerisable mesogenic compounds available to the expert. Other aims of the present invention are immediately evident to the person skilled in the art from the following detailed description.
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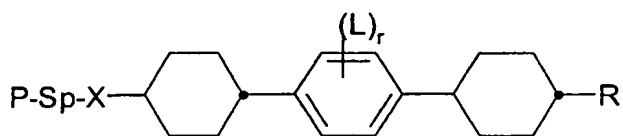
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It was found that these aims can be achieved by providing polymerisable 1,4-Di-(trans-cyclohexyl)benzenes according to the present invention.

5 Summary of the Invention

The present invention relates to polymerisable 1,4-di-(trans-cyclohexyl)benzenes of formula I

10



15 wherein

P is a polymerisable group,

Sp is a spacer group or a single bond,

20

X is -O-, -S-, -OCH₂-, -CH₂O-, -CO-, -COO-, -OCO-, -OCO-O-, -CO-NR⁰-, -NR⁰-CO-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -CH=CH-COO-, -OOC-CH=CH- or a single bond,

25

R is H, F, Cl, Br, I, CN, SCN, SF₅H, NO₂, or straight chain, branched or cyclic alkyl with 1 to 20 C-atoms, which may be unsubstituted, mono- or poly-substituted by F, Cl, Br, I or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -NR⁰-, -SiR⁰R⁰⁰-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, or denotes P-Sp-X,

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R⁰ and R⁰⁰ are independently of each other H or alkyl with 1 to 4 C atoms,

L is F, Cl, Br, I, CN, NO₂ or alkyl, alkoxy, alkylcarbonyl, alkoxy carbonyl or alkylcarbonlyoxy with 1 to 7 C atoms, wherein one or more H atoms may be substituted by F or Cl, and
5
r is 0, 1, 2, 3 or 4.

The invention further relates to polymerisable liquid crystal mixture comprising at least one compound of formula I.

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The invention further relates to an anisotropic polymer or polymer film prepared from one or more compounds of formula I or from a polymerisable liquid crystal mixture comprising at least one compound of formula I.

15
The invention further relates to the use of the polymerisable compounds of formula I, the polymerisable mixtures and polymers prepared thereof in optical films, polarisers, compensators, beam splitters, reflective films, alignment layers, colour filters, holographic
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elements, hot stamping foils, coloured images, decorative or security markings, liquid crystal pigments, adhesives, synthetic resins with anisotropic mechanical properties, cosmetics, diagnostics, nonlinear optics, optical information storage, as chiral dopants, in electronic devices like for example field effect transistors (FET) as components
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of integrated circuitry, as thin film transistors in flat panel display applications or for Radio Frequency Identification (RFID) tags, or in semiconducting components for organic light emitting diode (OLED) applications such as electroluminescent displays or backlights of e.g. liquid crystal displays, for photovoltaic or sensor devices, as
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electrode materials in batteries, as photoconductors, or for electrophotographic applications like electrophotographic recording.

The invention further relates to a liquid crystal display comprising in its active layer at least one compound of formula I or a mixture or
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polymer comprising at least one compound of formula I.

Definitions of Terms

5 The term 'film' as used in this application includes self-supporting, i.e. free-standing, films that show more or less pronounced mechanical stability and flexibility, as well as coatings or layers on a supporting substrate or between two substrates.

10 The term 'liquid crystal or mesogenic material' or 'liquid crystal or mesogenic compound' should denote materials or compounds comprising one or more rod-shaped, board-shaped or disk-shaped mesogenic groups, i.e. groups with the ability to induce liquid crystal phase behaviour. Liquid crystal compounds with rod-shaped or board-shaped groups are also known in the art as 'calamitic' liquid crystals. Liquid crystal compounds with a disk-shaped group are also
15 known in the art as 'discotic' liquid crystals. The compounds or materials comprising mesogenic groups do not necessarily have to exhibit a liquid crystal phase themselves. It is also possible that they show liquid crystal phase behaviour only in mixtures with other compounds, or when the mesogenic compounds or materials, or the
20 mixtures thereof, are polymerised.

For the sake of simplicity, the term 'liquid crystal material' is used hereinafter for both liquid crystal materials and mesogenic materials, and the term 'mesogen' is used for the mesogenic groups of the material.

25

Detailed Description of the Invention

The specific advantage of the compounds of formula I is that the 1,4-Di-(trans-cyclohexyl)benzene core, in particular when substituted
30 with one or more fluoro atoms, is very similar in structure to common low molar mass LC mixtures for TFT displays. As a result, the compounds of formula I show better solubility in LC media, higher stability and resistance to degradation, compared for example to ester based reactive mesogens known from prior art. Also, the
35 birefringence of the compounds of formula I is lower than in many

reactive mesogens known from prior art, making them more suitable in particular for use in low Δn TFT displays.

Particularly preferred are compounds of formula I, wherein

- 5 - R is P-Sp-X,
- R is F, Cl, CN or alkyl, alkoxy or alkenyl with 1 to 12 C-atoms which is optionally mono- or poly-substituted by F,
- r is 1 or 2,
- 10 - r is 1 or 2 and L is F,
- Sp is alkylene with 1 to 12 C atoms which is optionally mono- or polysubstituted by F and wherein one or more non-adjacent CH₂ may be replaced, in each case independently from one another, by -O-, -CH=CH- or -C≡C-,
- 15 - X is -O-, -COO-, -OCO-, -OCOO- or a single bond.

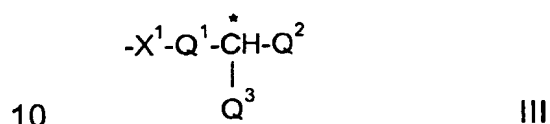
20 L in formula I is preferably F, Cl, CN, OH, NO₂, CH₃, C₂H₅, OCH₃, OC₂H₅, COCH₃, COC₂H₅, COOCH₃, COOC₂H₅, CF₃, OCF₃, OCHF₂ or OC₂F₅, in particular F, Cl, CN, CH₃, C₂H₅, OCH₃, COCH₃ or OCF₃, most preferably F, Cl, CH₃, OCH₃ or COCH₃.

25 If R in formula I is an alkyl or alkoxy radical, i.e. where the terminal CH₂ group is replaced by -O-, this may be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, or octoxy, furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy, for example.

35 Oxaalkyl, i.e. where one CH₂ group is replaced by -O-, is preferably straight-chain 2-oxapropyl (=methoxymethyl), 2- (=ethoxymethyl) or 3-oxabutyl (=2-methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl,

2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, for example.

5 In the compounds of formula I R may be an achiral or a chiral group.
In case of a chiral group it is preferably selected according to the following formula III:



wherein

15 X^1 is -O-, -S-, -CO-, -COO-, -OCO-, -OCOO- or a single bond,

Q^1 is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond,

20 Q^2 is an alkyl or alkoxy group with 1 to 10 C atoms which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH_2 groups to be replaced, in each case independently from one another, by - $\text{C}\equiv\text{C}$ -, -O-, -S-, -NH-, - $\text{N}(\text{CH}_3)$ -, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO- or -CO-S- in such a manner that oxygen atoms are not
25 linked directly to one another,

Q^3 is halogen, a cyano group or an alkyl or alkoxy group with 1 to 4 C atoms different from Q^2 .

30 In case Q^1 in formula III is an alkylene-oxy group, the O atom is preferably adjacent to the chiral C atom.

Preferred chiral groups R are 2-butyl (=1-methylpropyl), 2-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, 2-octyl, in particular 2-methylbutyl, 2-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy, 2-



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octyloxy, 2-oxa-3-methylbutyl, 3-oxa-4-methylpentyl, 4-methylhexyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-methoxyoctoxy, 6-methyloctoxy, 6-methyloctanoyloxy, 5-methylheptyloxycarbonyl, 2-methylbutyryloxy, 3-methylvaleroyloxy, 4-methylhexanoyloxy, 2-chloropropionyloxy, 2-chloro-3-methylbutyryloxy, 2-chloro-4-methylvaleryloxy, 2-chloro-3-methylvaleryloxy, 2-methyl-3-oxapentyl, 2-methyl-3-oxahexyl, 1-methoxypropyl-2-oxy, 1-ethoxypropyl-2-oxy, 1-propoxypropyl-2-oxy, 1-butoxypropyl-2-oxy, 2-fluorooctyloxy, 2-fluorodecyloxy for example.

In addition, compounds of formula I containing an achiral branched group R may occasionally be of importance, for example, due to a reduction in the tendency towards crystallization. Branched groups of this type generally do not contain more than one chain branch. Preferred achiral branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl (=3-methylbutyl), isopropoxy, 2-methylpropoxy and 3-methylbutoxy.

Halogen is preferably F or Cl.

The polymerisable group P is preferably selected from

$\text{CH}_2=\text{CW}^1\text{-COO-}$, $\text{W}^2\text{HC}-\text{CH}-$  CH- , W^2  $(\text{CH}_2)_k\text{-O-}$, $\text{CH}_2=\text{CW}^2\text{-(O)}_{k1}\text{-}$, $\text{CH}_3\text{-CH=CH-O-}$, $\text{HO-CW}^2\text{W}^3\text{-}$, $\text{HS-CW}^2\text{W}^3\text{-}$, $\text{HW}^2\text{N-}$, $\text{HO-CW}^2\text{W}^3\text{-NH-}$, $\text{CH}_2=\text{CW}^1\text{-CO-NH-}$, $\text{CH}_2=\text{CH-(COO)}_{k1}\text{-Phe-(O)}_{k2}\text{-}$, Phe-CH=CH- , HOOC- , OCN- and $\text{W}^4\text{W}^5\text{W}^6\text{Si-}$, with W^1 being H, Cl, CN, phenyl or alkyl with 1 to 5 C-atoms, in particular H, Cl or CH_3 , W^2 and W^3 being independently of each other H or alkyl with 1 to 5 C-atoms, in particular methyl, ethyl or n-propyl, W^4 , W^5 and W^6 being independently of each other Cl, oxaalkyl or oxacarbonylalkyl with 1 to 5 C-atoms, Phe being 1,4-phenylene and k_1 and k_2 being independently of each other 0 or 1.

Especially preferably P is a vinyl group, an acrylate group, a methacrylate group, a propenyl ether group or an epoxy group, especially preferably an acrylate or a methacrylate group.

As for the spacer group Sp all groups can be used that are known for this purpose to those skilled in the art. The spacer group Sp is preferably a linear or branched alkylene group having 1 to 20 C atoms, in particular 1 to 12 C atoms, in which, in addition, one or more non-adjacent CH₂ groups may be replaced by -O-, -S-, -NH-, -N(CH₃)-, -CO-, -O-CO-, -S-CO-, -O-COO-, -CO-S-, -CO-O-, -CH(halogen)-, -C(halogen)₂-, -CH(CN)-, -CH=CH- or -C≡C-, or a siloxane group.

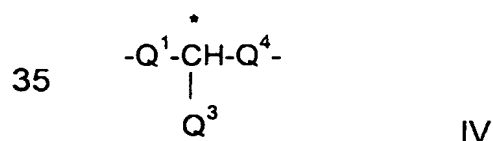
Typical spacer groups are for example -(CH₂)_p-, -(CH₂CH₂O)_r-CH₂CH₂-, -CH₂CH₂-S-CH₂CH₂- or -CH₂CH₂-NH-CH₂CH₂- or -(SiR⁰R⁰⁰-O)_p-, with p being an integer from 2 to 12, r being an integer from 1 to 3 and R⁰ and R⁰⁰ having the meanings given in formula I.

Preferred spacer groups are ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, ethyleneoxyethylene, methyleneoxybutylene, ethylene-thioethylene, ethylene-N-methyl-iminoethylene, 1-methylalkylene, ethenylene, propenylene and butenylene for example.

Further preferred are compounds with one or two groups P-Sp-X wherein Sp and/or X is a single bond.

In case of compounds with two groups P-Sp-X, each of the two polymerisable groups P, the two spacer groups Sp, and the two linkage groups X can be identical or different.

In another preferred embodiment of the invention the chiral compounds of formula I comprise at least one spacer group Sp that is a chiral group of formula IV:



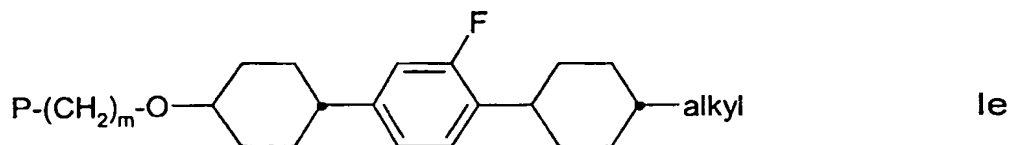
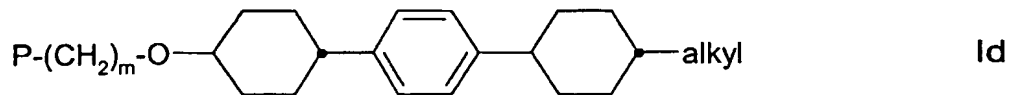
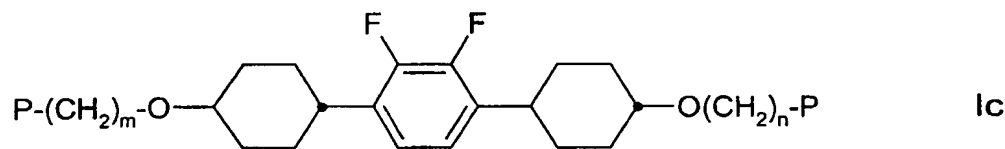
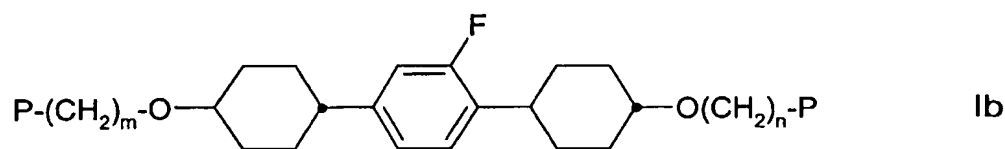
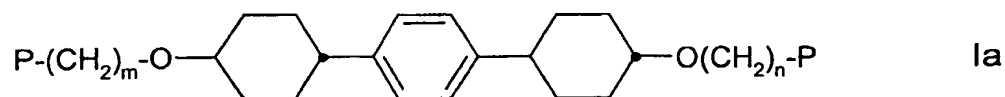
wherein

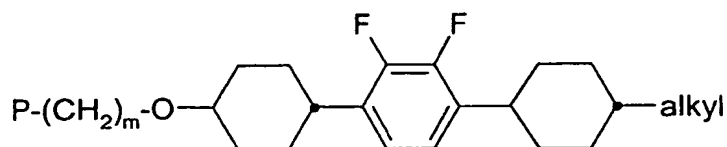
Q^1 and Q^3 have the meanings given in formula III, and

Q^4 is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond, being different from Q^1 .

Especially preferred are the following compounds:

Particularly preferred compounds of formula I are those of the following formulae





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wherein P has one of the meanings given above, and is especially preferably acryl, methacryl or vinyloxy, m and n are identical or different integers from 1 to 12, and alkyl is straight chain alkyl with 1 to 8 C atoms.

10

The compounds of formula I can be synthesized according to or in analogy to methods which are known per se and which are described in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart. Some specific methods of preparation can be taken from the examples.

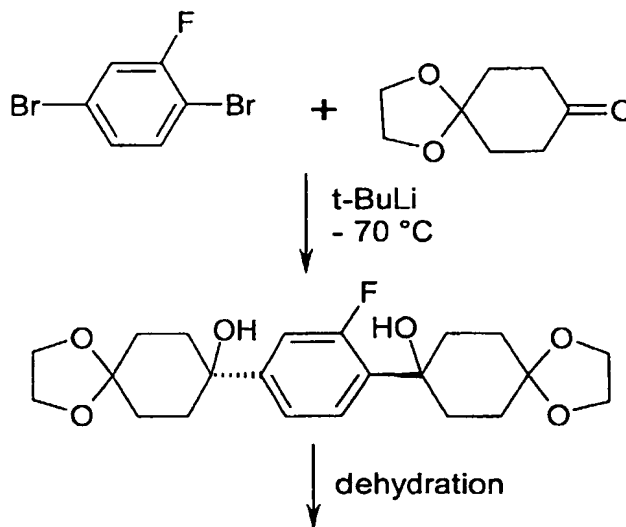
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Furthermore, the compounds of formula I can be synthesized according to or in analogy to the following reaction schemes:

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Scheme 1:

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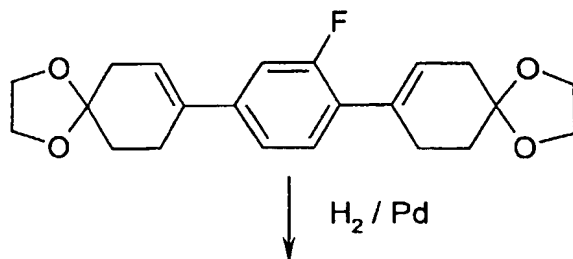


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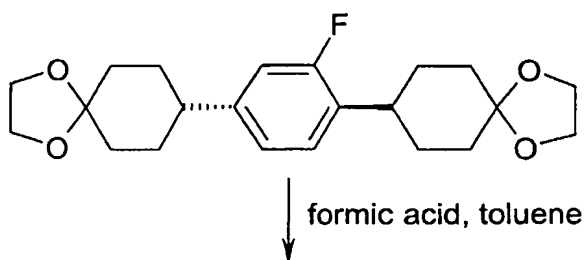
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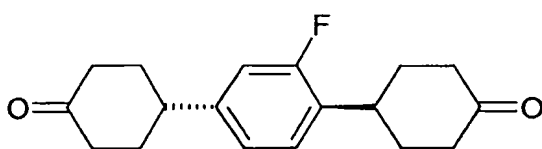
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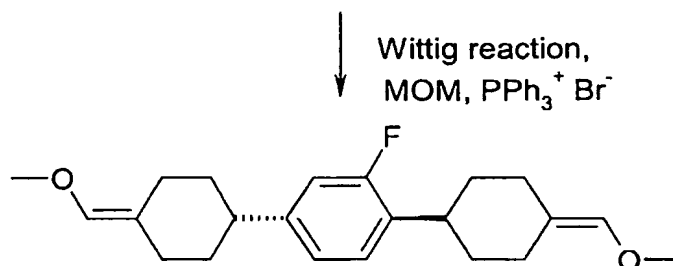
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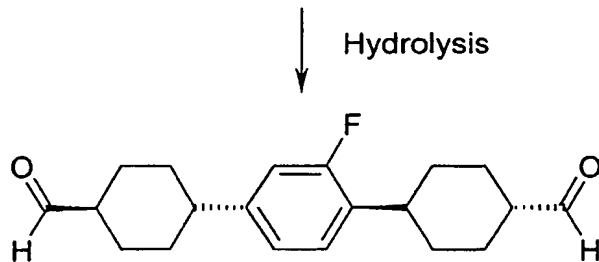
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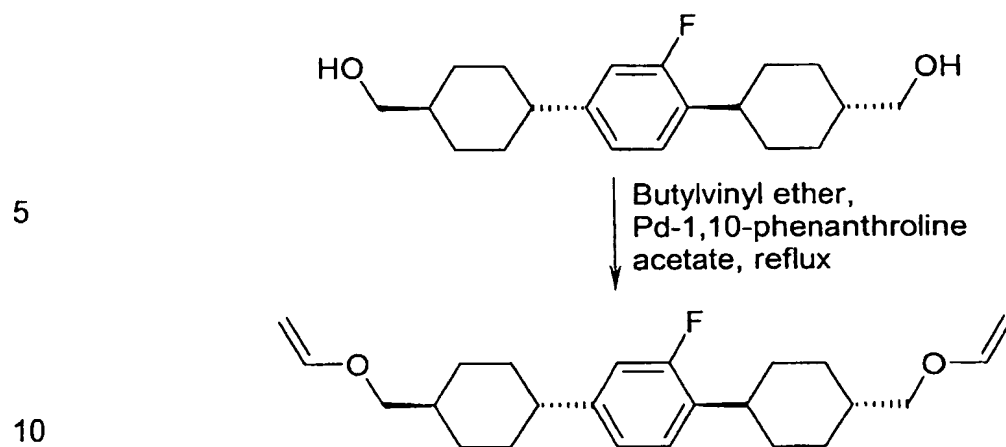
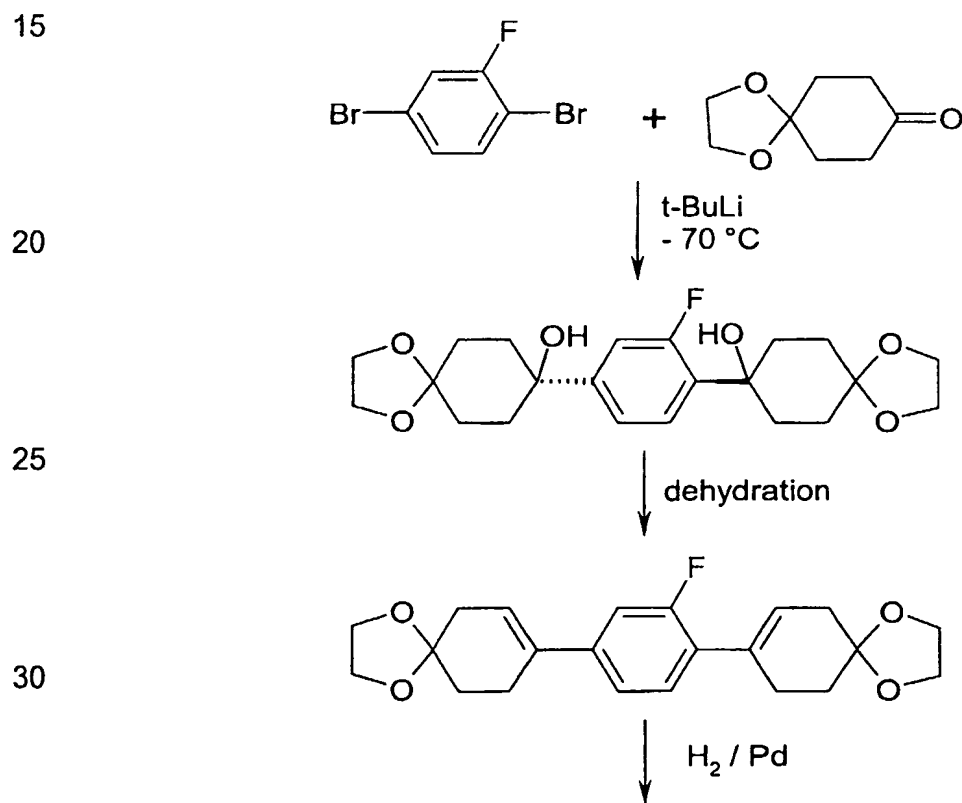


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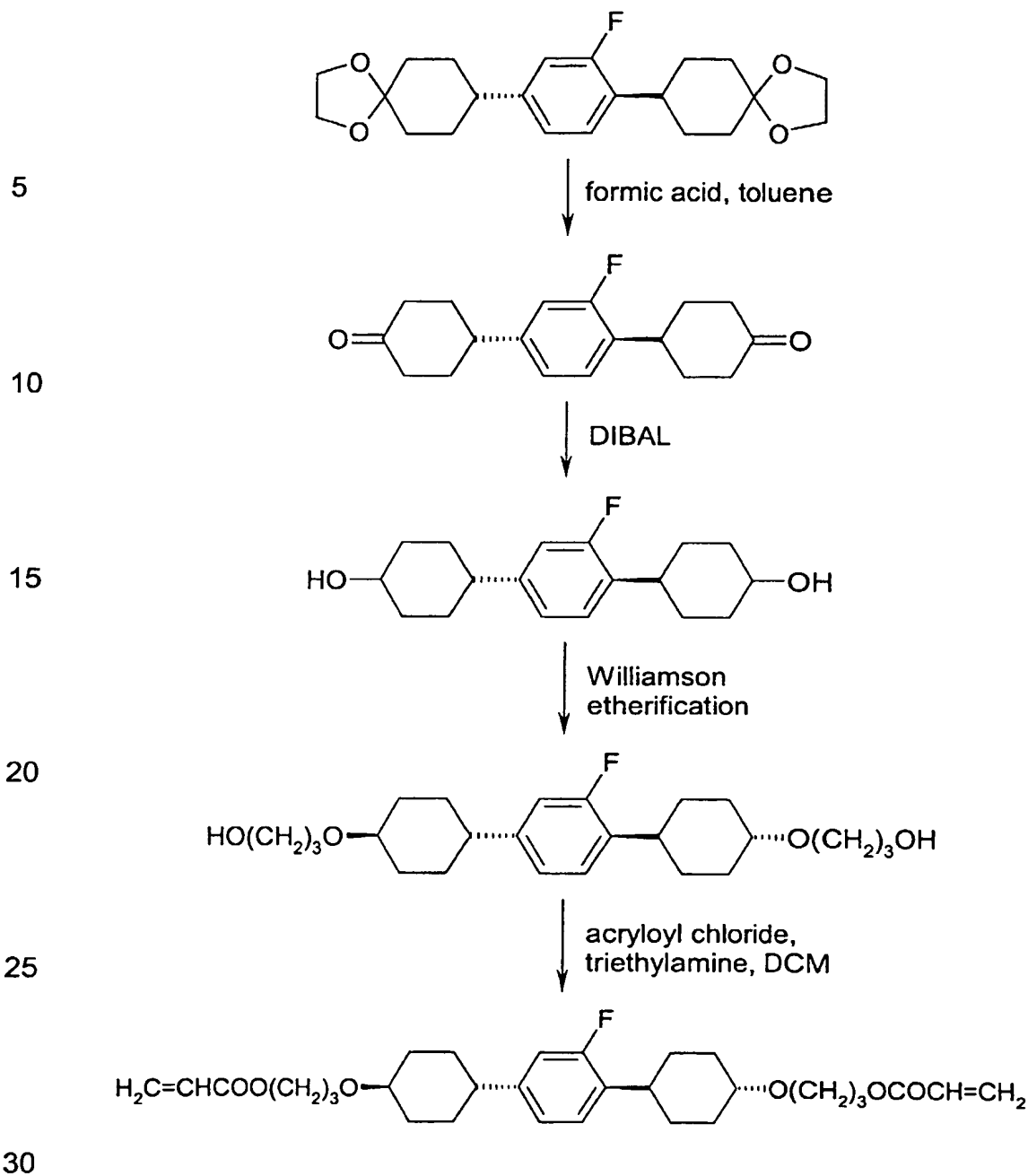


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Scheme 2:

- 15 -



The compounds of formula I can be used in a liquid crystal mixture for displays like, for example, TN or STN displays, active matrix displays, displays of the IPS (in plane switching) or VA (vertically aligned) mode like VAN (vertically aligned nematic) or VAC (vertically aligned cholesteric), displays of the ECB (electrically controlled

5 birefringence), DAP (deformation of aligned phases), CSH (colour super homeotropic) or ASM (axially symmetric microcell) mode, phase-change, guest-host, flexoelectric, ferroelectric displays, bistable nematic and cholesteric displays like PSCT (polymer stabilized cholesteric texture), or PDLC, polymer gel or polymer network displays.

10 In particular, the polymerisable compounds of formula I and mixtures comprising them are useful for liquid crystal displays that comprise a polymer or polymer network component for the purpose of assisting alignment, mesophase stability and/or electrooptical property improvement, in particular to achieve faster response times and/or lower threshold voltages, or for the purpose to create a multidomain structure to achieve improved contrast at wide viewing angles. Such
15 displays are for example of the TN, STN, ECB, VA, IPS, multidomain or hybrid mode, and are described for example in US 5,189,540, US 6,177,972, EP 0 903 392, and Hasebe et al., Jpn.J.Appl.Phys.1994, 33, 6245.

20 Furthermore, the compounds of formula I are suitable as polymerisable component in active broadband polymer stabilized liquid crystal displays as described for example in H. Guillard and P. Sixou, *Liq.Cryst.* (2001) **28(6)**, 933, the entire disclosure of which is incorporated into this application by reference. These displays
25 comprise an active cholesteric layer with a broadened reflection wavelength band that is switchable between a planar reflective, a scattering and a homeotropic transparent state.

30 The compounds of formula I are also suitable as a polymer component in polymer stabilised displays, such as bistable PSCT (polymer stabilized cholesteric texture) displays, or PDLC or polymer gel displays of the scattering type. Anisotropic polymer gels and displays comprising them are disclosed for example in DE 195 04 224, GB 2 279 659, WO 93/22397, US 5,538,768, US 5,543,075 and
35 EP 0 451 905

Thus, another aspect of the invention is a liquid crystal mixture, in particular a nematic liquid crystal mixture, comprising at least one compound of formula I.

- 5 Another aspect of the invention is a liquid crystal display comprising a liquid crystal medium containing at least one compound of formula I.

For the applications described above the liquid crystal mixture preferably contains at least one compound of formula I, and a
10 nematic host mixture comprising one or more nematic or nematogenic compounds.

Preferably the liquid crystal mixture consists of 2 to 25, preferably 3 to 15 compounds, at least one of which is a compound of formula I.
15 The other compounds, forming the nematic host mixture, are preferably low molecular weight liquid crystal compounds selected from nematic or nematogenic substances, for example from the known classes of the azoxybenzenes, benzylidene-anilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or
20 cyclohexyl esters of cyclohexanecarboxylic acid, phenyl or cyclohexyl esters of cyclohexylbenzoic acid, phenyl or cyclohexyl esters of cyclohexylcyclohexanecarboxylic acid, cyclohexylphenyl esters of benzoic acid, of cyclohexanecarboxylic acid and of cyclohexylcyclohexanecarboxylic acid, phenylcyclohexanes, cyclohexyl-
25 biphenyls, phenylcyclohexylcyclohexanes, cyclohexylcyclohexanes, cyclohexylcyclohexenes, cyclohexylcyclohexylcyclohexenes, 1,4-bis-cyclohexylbenzenes, 4,4'-bis-cyclohexylbiphenyls, phenyl- or cyclohexylpyrimidines, phenyl- or cyclohexylpyridines, phenyl- or cyclohexylpyridazines, phenyl- or cyclohexyldioxanes, phenyl- or cyclohexyl-
30 hexyl-1,3-dithianes, 1,2-diphenyl-ethanes, 1,2-dicyclohexylethanes, 1-phenyl-2-cyclohexylethanes, 1-cyclohexyl-2-(4-phenylcyclohexyl)-ethanes, 1-cyclohexyl-2-biphenyl-ethanes, 1-phenyl-2-cyclohexylphenylethanes, optionally halogenated stilbenes, benzyl phenyl ether, tolanes, substituted cinnamic acids and further classes of
35 nematic or nematogenic substances. The 1,4-phenylene groups in these compounds may also be laterally mono- or difluorinated.

The liquid crystal mixture of this preferred embodiment is based on the achiral compounds of this type.

- 5 The most important compounds that are possible as components of these liquid crystal mixtures can be characterized by the following formula



10

wherein L' and E, which may be identical or different, are in each case, independently from one another, a bivalent radical from the group formed by -Phe-, -Cyc-, -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -Pyr-, -Dio-, -B-Phe- and -B-Cyc- and their mirror images, where Phe is unsubstituted or fluorine-substituted 1,4-phenylene, Cyc is trans-1,4-cyclohexylene or 1,4-cyclohexenylene, Pyr is pyrimidine-2,5-diyl or pyridine-2,5-diyl, Dio is 1,3-dioxane-2,5-diyl and B is 2-(trans-1,4-cyclohexyl)ethyl, pyrimidine-2,5-diyl, pyridine-2,5-diyl or 1,3-dioxane-2,5-diyl.

20

G' in these compounds is selected from the following bivalent groups -CH=CH-, -N(O)N-, -CH=CY-, -CH=N(O)-, -C≡C-, -CH₂-CH₂-, -CO-O-, -CH₂-O-, -CO-S-, -CH₂-S-, -CH=N-, -COO-Phe-COO- or a single bond, with Y being halogen, preferably chlorine, or -CN.

25

R' and R'' are, in each case, independently of one another, alkyl, alkenyl, alkoxy, alkenyloxy, alkanoyloxy, alkoxycarbonyl or alkoxycarbonyloxy with 1 to 18, preferably 3 to 12 C atoms, or alternatively one of R' and R'' is F, CF₃, OCF₃, Cl, NCS or CN.

30

In most of these compounds R' and R'' are, in each case, independently of each another, alkyl, alkenyl or alkoxy with different chain length, wherein the sum of C atoms in nematic media generally is between 2 and 9, preferably between 2 and 7.

35

Many of these compounds or mixtures thereof are commercially available. All of these compounds are either known or can be prepared by methods which are known per se, as described in the literature (for example in the standard works such as Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart), to be precise under reaction conditions which are known and suitable for said reactions. Use may also be made here of variants which are known per se, but are not mentioned here.

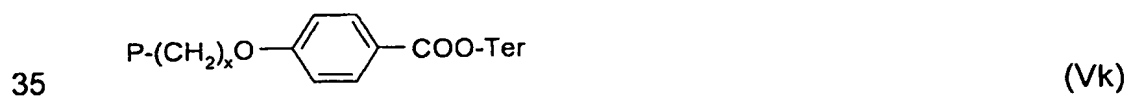
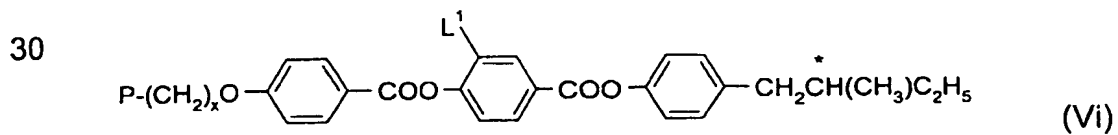
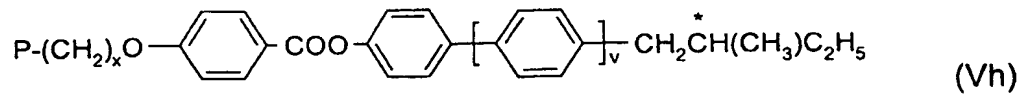
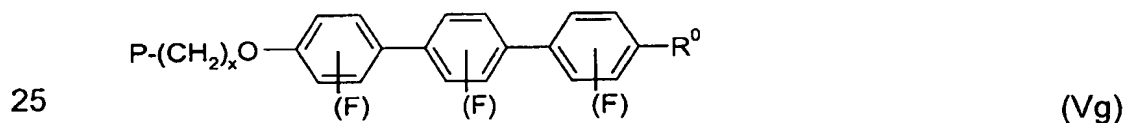
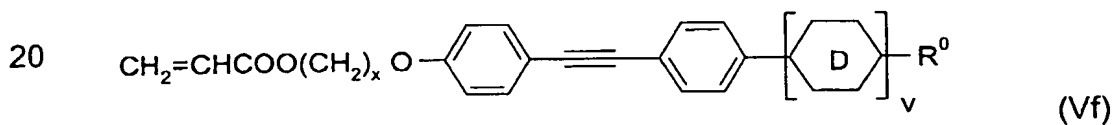
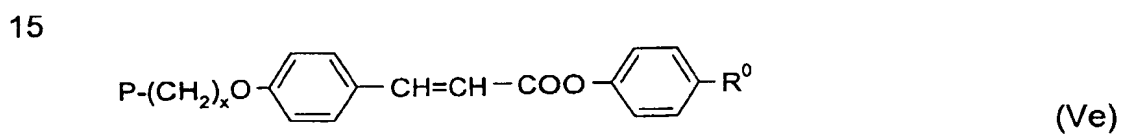
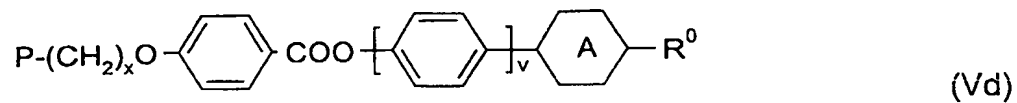
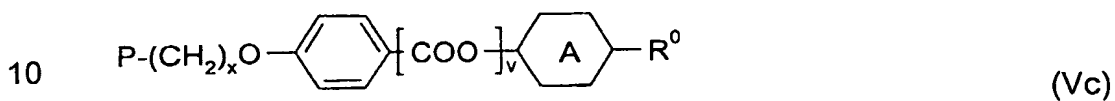
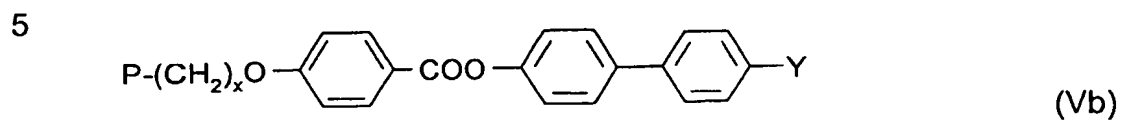
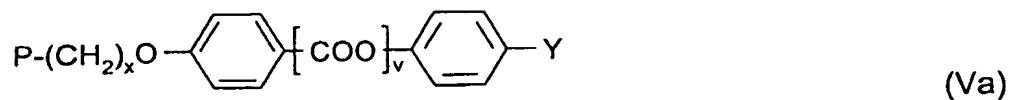
The compounds of formula I and polymerisable liquid crystal mixtures comprising them are further useful for the preparation of anisotropic polymer films or coatings.

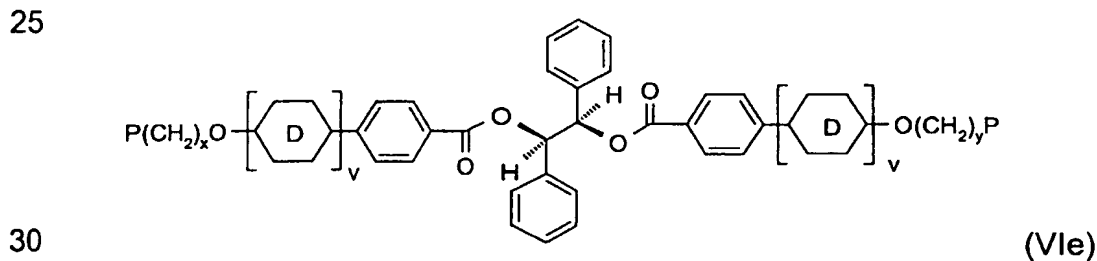
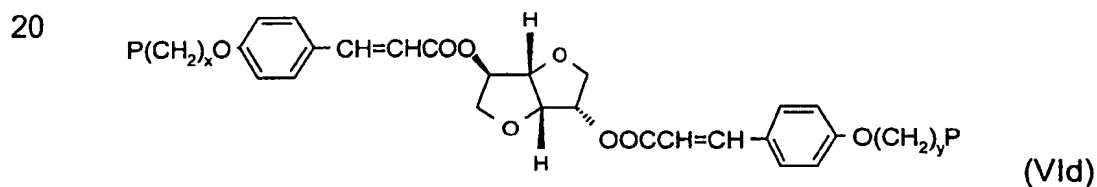
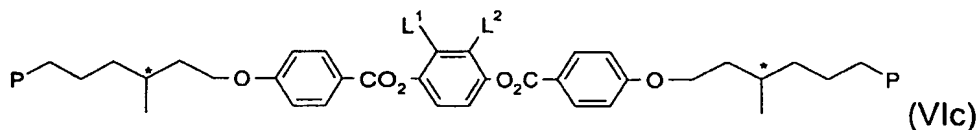
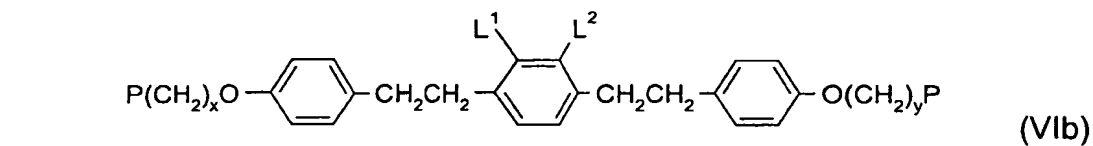
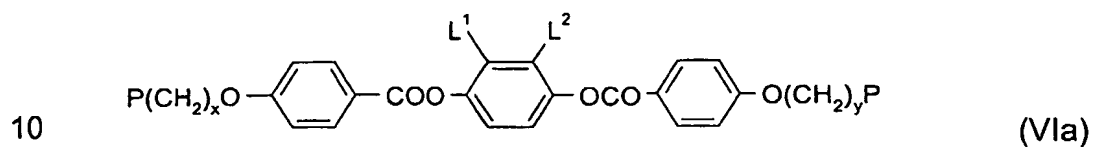
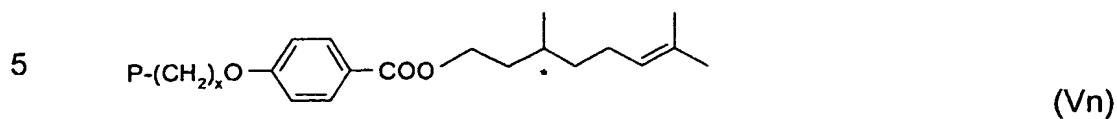
For the preparation of anisotropic polymer gels or polymer films, the liquid crystal mixture should comprise at least one polymerisable compound, which can be a compound of formula I or an additional polymerisable mesogenic or liquid crystalline compound.

Examples of suitable polymerisable mesogenic compounds that can be used as comonomers together with the compounds of formula I in a polymerisable liquid crystal mixture, are disclosed for example in WO 93/22397; EP 0,261,712; DE 195,04,224; WO 95/22586 and WO 97/00600. The compounds disclosed in these documents, however, are to be regarded merely as examples that shall not limit the scope of this invention.

Preferably the polymerizable liquid crystal mixture comprises at least one polymerisable mesogenic compound having one polymerisable functional group and at least one polymerisable mesogenic compound having two or more polymerisable functional groups.

Examples of especially useful chiral and achiral polymerisable mesogenic compounds are shown in the following lists which should, however, be taken only as illustrative and is in no way intended to restrict, but instead to explain the present invention:





wherein P has one of the meanings of formula I and its preferred meanings as mentioned above, x and y are identical or different integers from 1 to 12, A and D are 1,4-phenylene or 1,4-cyclohexylene, v is 0 or 1, Y is a polar group, R⁰ is a non-polar alkyl or alkoxy group, Ter is a terpenoid radical like e.g. menthyl, Chol is a

cholesteryl group, and L^1 and L^2 are each independently H, F, Cl, OH, CN, NO_2 or optionally alkyl, alkoxy, alkylcarbonyl or alkoxy carbonyl with 1 to 7 C atoms.

- 5 The term 'polar group' in this connection means a group selected from F, Cl, CN, NO_2 , OH, OCH_3 , OCN, SCN, an optionally fluorinated carbonyl or carboxyl group with up to 4 C atoms or a mono- oligo- or polyfluorinated alkyl or alkoxy group with 1 to 4 C atoms. The term 'non-
10 polar group' means an alkyl group with 1 or more, preferably 1 to 12 C atoms or an alkoxy group with 2 or more, preferably 2 to 12 C atoms.

15 The polymerisable liquid crystal mixture may also comprise one or more non-reactive chiral dopants in addition or alternatively to chiral polymerisable mesogenic compounds. Typically used chiral dopants are e.g. the commercially available R or S 811, R or S 1011, R or S 2011 or CB 15 (from Merck KGaA, Darmstadt, Germany).

20 Very preferred are chiral dopants with a high helical twisting power (HTP), in particular dopants comprising a sorbitol group as described in WO 98/00428, dopants comprising a hydrobenzoin group as described in GB 2,328,207, chiral binaphthyl derivatives as described in EP 01111954.2, chiral binaphthol acetal derivatives as described in EP 01104842.8, chiral TADDOL derivatives as described in WO 02/06265, and chiral dopants with at least one fluorinated linkage
25 group and a terminal or central chiral group as described in WO 02/06196 and WO 02/06195.

30 To prepare anisotropic polymer films, the polymerisable liquid crystal is preferably coated onto a substrate, aligned and polymerised in situ, for example by exposure to heat or actinic radiation, to fix the orientation of the liquid crystal molecules. Alignment and curing are carried out in the liquid crystalline phase of the mixture.

35 The substrate is for example a glass or quartz sheet or a plastic film or sheet, and can be removed after polymerisation or not. Suitable plastic substrates are for example polyethyleneterephthalate (PET),

of polyvinylalcohol (PVA), polycarbonate (PC) or triacetylcellulose (TAC). The polymerisable chiral LC material may also be dissolved or dispersed in an organic solvent that is evaporated before or during polymerisation.

5

Alignment of the liquid crystal material can be achieved for example by treatment of the substrate onto which the material is coated, by shearing the material during or after coating, by application of a magnetic or electric field to the coated material, or by the addition of surface-active compounds to the liquid crystal material. Reviews of alignment techniques are given for example by I. Sage in "Thermotropic Liquid Crystals", edited by G. W. Gray, John Wiley & Sons, 1987, pages 75-77, and by T. Uchida and H. Seki in "Liquid Crystals - Applications and Uses Vol. 3", edited by B. Bahadur, World Scientific Publishing, Singapore 1992, pages 1-63. A review of alignment materials and techniques is given by J. Cognard, Mol. Cryst. Liq. Cryst. 78, Supplement 1 (1981), pages 1-77.

Polymerisation takes place by exposure to heat or actinic radiation. Actinic radiation means irradiation with light, like UV light, IR light or visible light, irradiation with X-rays or gamma rays or irradiation with high energy particles, such as ions or electrons. Preferably polymerisation is carried out by UV irradiation at a non-absorbing wavelength. As a source for actinic radiation for example a single UV lamp or a set of UV lamps can be used. When using a high lamp power the curing time can be reduced. Another possible source for actinic radiation is a laser, like e.g. a UV laser, an IR laser or a visible laser.

Polymerisation is carried out in the presence of an initiator absorbing at the wavelength of the actinic radiation. For example, when polymerising by means of UV light, a photoinitiator can be used that decomposes under UV irradiation to produce free radicals or ions that start the polymerisation reaction. When curing polymerisable mesogens with acrylate or methacrylate groups, preferably a radical photoinitiator is used, when curing polymerisable mesogens vinyl and

epoxide groups, preferably a cationic photoinitiator is used. It is also possible to use a polymerisation initiator that decomposes when heated to produce free radicals or ions that start the polymerisation.

5 As a photoinitiator for radical polymerisation for example the commercially available Irgacure 651, Irgacure 184, Darocure 1173 or Darocure 4205 (all from Ciba Geigy AG) can be used, whereas in case of cationic photopolymerisation the commercially available UVI 6974 (Union Carbide) can be used.

10 The polymerisable material can additionally comprise one or more other suitable components such as, for example, catalysts, sensitizers, stabilizers, inhibitors, chain-transfer agents, co-reacting monomers, surface-active compounds, lubricating agents, wetting agents, dispersing agents, hydrophobing agents, adhesive agents, flow improvers,
15 defoaming agents, deaerators, diluents, reactive diluents, auxiliaries, colourants, dyes or pigments.

Compounds of formula I comprising a chiral group are suitable as chiral dopants.

20 Furthermore, the compounds of formula I are suitable as comonomers for liquid crystal materials with semiconductor or charge carrier properties, which can be used in electronic devices like for example field effect transistors (FET) as components of integrated circuitry, as thin film transistors in flat panel display applications or for Radio Frequency
25 Identification (RFID) tags, or semiconducting components for organic light emitting diode (OLED) applications such as electroluminescent displays or backlights of e.g. liquid crystal displays, photovoltaic or sensor devices, photoconductors, or electrophotographic applications
30 like electrophotographic recording devices.

For example, semiconductors comprising polymerisable liquid crystal compounds are disclosed in WO 00/79617, JP-A-2000-347432, JP-A-11-209761, Sirringhaus et al., Appl. Phys. Lett., 77(3) (2000) 406-408, ,
35 and Grell et al., J. Korean Phys. Soc. 2000, 36(6), 331. Electroluminescent devices using liquid crystal materials are described

for example in WO 95/17018 and WO 95/04306. Organic photoconductors with liquid crystal properties are described for example in EP 0 563 768 and EP 0 527 376.

5 Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following examples are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever.

10

In the foregoing and in the following examples, unless otherwise indicated, all temperatures are set forth uncorrected in degrees Celsius and all parts and percentages are by weight.

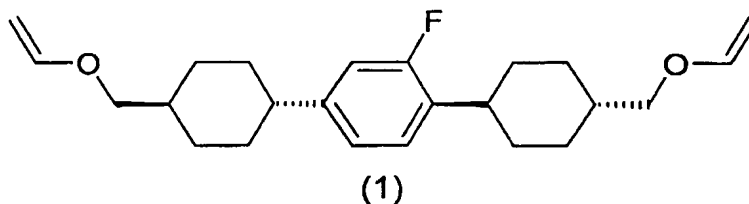
15 The following abbreviations are used to illustrate the liquid crystalline phase behaviour of the compounds: K = crystalline; N = nematic; S = smectic; Ch = cholesteric; I = isotropic. The numbers between the symbols indicate the phase transition temperatures in ° C. Furthermore, Δn is the optical anisotropy measured at 20 °C and 589 nm, $\Delta\epsilon$ is the dielectric anisotropy at 20 °C and 1 kHz.

20

Example 1

Compound (1) is prepared according to reaction scheme 1.

25



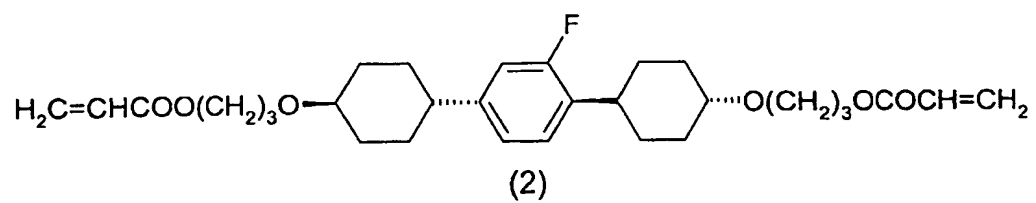
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Example 2

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Compound (2) is prepared according to reaction scheme 2.

- 26 -



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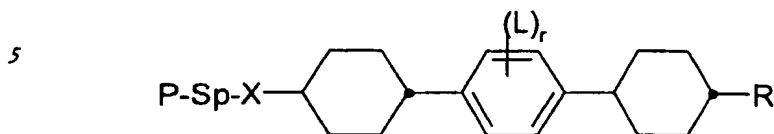
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Claims

1. A polymerisable compound of formula I



wherein

P is a polymerisable group,

Sp is a spacer group or a single bond,

X is -O-, -S-, -OCH₂-, -CH₂O-, -CO-, -COO-, -OCO-, -OCO-O-, -CO-NR⁰-, -NR⁰-CO-, -OCH₂-, -CH₂O-, -SCH₂-, -CH₂S-, -CH=CH-COO-, -OOC-CH=CH- or a single bond,

R is H, F, Cl, Br, I, CN, SCN, SF₅H, NO₂, or straight chain, branched or cyclic alkyl with 1 to 20 C-atoms, which may be unsubstituted, mono- or poly-substituted by F, Cl, Br, I or CN, it being also possible for one or more non-adjacent CH₂ groups to be replaced, in each case independently from one another, by -O-, -S-, -NH-, -NR⁰-, -SiR⁰R⁰⁰-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO-, -CO-S-, -CH=CH- or -C≡C- in such a manner that O and/or S atoms are not linked directly to one another, or denotes P-Sp-X,

R⁰ and R⁰⁰ are independently of each other H or alkyl with 1 to 4 C atoms,

L is F, Cl, Br, I, CN, NO₂ or alkyl, alkoxy, alkylcarbonyl, alkoxycarbonyl or alkylcarbonyloxy with 1 to 7 C atoms,

wherein one or more H atoms may be substituted by F or Cl, and

5 r is 0, 1, 2, 3 or 4.

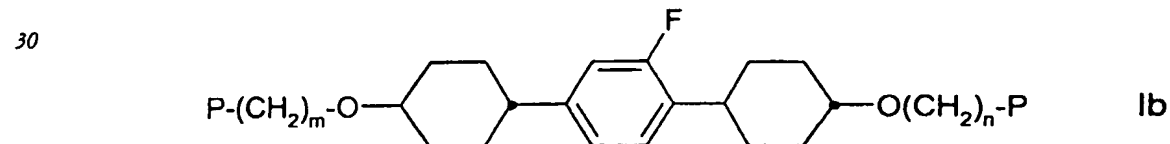
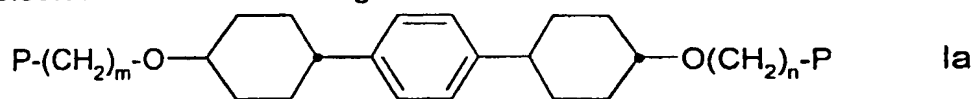
2. A polymerisable compound according to claim 1, wherein R is P-Sp-X.

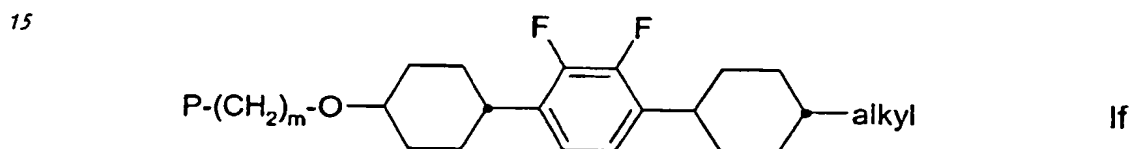
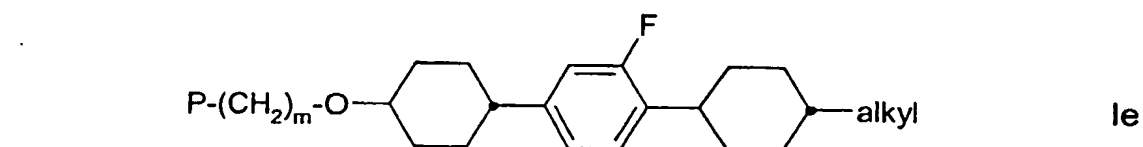
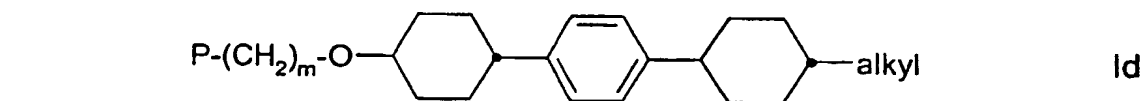
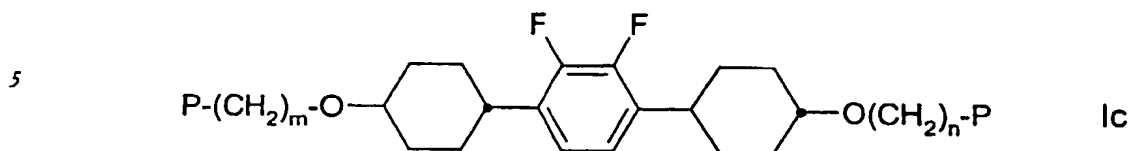
10 3. A polymerisable compound according to claim 1 or 2, wherein r is 1 or 2 and L is F, Cl, CN, OH, NO₂, CH₃, C₂H₅, OCH₃, OC₂H₅, COCH₃, COC₂H₅, COOCH₃, COOC₂H₅, CF₃, OCF₃, OCHF₂ or OC₂F₅.

15 4. A polymerisable compound as claimed in any of claims 1 to 3, wherein P is a vinyl, acrylate, a methacrylate, a propenyl ether or epoxy group.

20 5. A polymerisable compound as claimed in any of claims 1 to 4, wherein Sp is alkylene with 1 to 12 C atoms which is optionally mono- or polysubstituted by F and wherein one or more non-adjacent CH₂ may be replaced, in each case independently from one another, by -O-, -CH=CH- or -C≡C-, and X is -O-, -COO-, -OCO-, -OCOO- or a single bond.

25 6. A polymerisable compound as claimed in any of claims 1 to 4, selected from the following formulae





wherein P is as defined in claim 1, m and n are identical or different integers from 1 to 12, and alkyl is straight chain alkyl with 1 to 8 C atoms.

- 25 7. A polymerisable compound obtained by a reaction scheme as hereinbefore described in Example 1 or 2.
8. A polymerisable liquid crystal mixture comprising at least one compound as claimed in any of claims 1 to 7.
- 30 9. An anisotropic polymer or polymer film obtained from a polymerisable liquid crystal mixture as claimed in claim 8.

10. Use of a polymerisable compound as claimed in any of claims 1 to 7, a mixture according to claim 8 or a polymer or polymer film according to claim 9 in optical films, polarisers, compensators, beam splitters, reflective films, alignment layers, colour filters, holographic elements, hot stamping foils, coloured images, decorative or security markings, liquid crystal pigments, adhesives, synthetic resins with anisotropic mechanical properties, cosmetics, diagnostics, nonlinear optics, optical information storage, as chiral dopants, in electronic devices like for example field effect transistors (FET) as components of integrated circuitry, as thin film transistors in flat panel display applications or for Radio Frequency Identification (RFID) tags, or in semiconducting components for organic light emitting diode (OLED) applications such as electroluminescent displays or backlights of e.g. liquid crystal displays, for photovoltaic or sensor devices, as electrode materials in batteries, as photoconductors, or for electrophotographic applications like electrophotographic recording.
11. A liquid crystal display comprising in its active layer at least one compound as claimed in any of claims 1 to 7, a mixture according to claim 8 or a polymer or polymer film according to claim 9.



INVESTOR IN PEOPLE

Application No: GB 0217907.5
Claims searched: 1-11

Examiner: Diane Davies
Date of search: 13 January 2003

Patents Act 1977 : Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-5, 8-11	WO 9813321 A (Chisso Corp) Whole document: liquid crystal compounds where P-Sp-X and R are alkenyl.
X	1-5, 8-11	WO 9808791 A (Chisso Corp) Whole document: liquid crystal compounds where P-Sp-X and R are alkenyl optionally substituted by fluorine.
X	1-5, 8-11	WO 9307234 A (Hoffman-La Roche AG) Whole document: liquid crystal compounds where P-Sp-X is chlorovinyl and R is alkyl.
X	1-5, 8-11	Chem. Abs. 137:54741 & DE 10157670 A (Merck Patent GmbH). M. Bremer et al, "Tetracyclic compound showing negative dielectric anisotropy and liquid crystal mixture suitable for liquid crystal display". See RN 438000 series of compounds.
X	1-5, 8-11	Chem. Abs. 131:221539 & JP 11241068 A (Dainippon Ink and Chemicals, Inc.) H. Ohnishi et al, "Nematic liquid crystal composition and liquid crystal display device using it".
X	1-5, 8-11	Chem. Abs. 123:270892 & DE 4426799 A (Merck Patent GmbH). V. Reiffenrath et al, "Fluorobenzene derivative and liquid-crystal medium". See compound 163004-85-1

Categories:

X Document indicating lack of novelty or inventive step	A Document indicating technological background and/or state of the art.
Y Document indicating lack of inventive step if combined with one or more other documents of same category.	P Document published on or after the declared priority date but before the filing date of this invention.
& Member of the same patent family	E Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^v:

C2C



INVESTOR IN PEOPLE

Application No: GB 0217907.5
Claims searched: 1-11

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Date of search: 13 January 2003

Worldwide search of patent documents classified in the following areas of the IPC:

C09K

The following online and other databases have been used in the preparation of this search report:

CAS-ONLINE, EPODOC, JAPIO, WPI